

## Kohlrausch law on independent migration of ions

# It depend only  $\infty$ -dilution

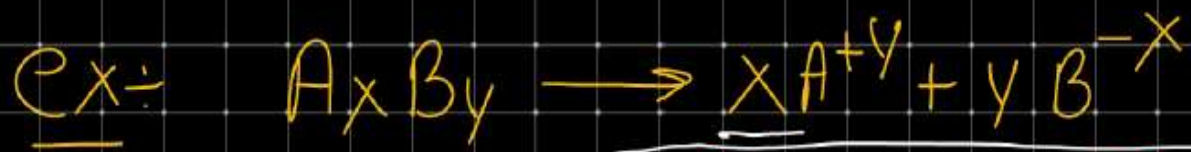
# It is applicable both strong & weak electrolyte.

# At infinite dilution dissociation of electrolyte is complete then each ion make a definite contribution towards equivalent conductance of electrolyte irrespective of other ion

# It's law state that, at  $\infty$ -dilution

Equivalent Conductance of electrolyte is sum of Equivalent Conductance of

Cation and anion. at  $\infty$ -dilution



Kohlrausch law

V.f. of  $A_x B_y$   
 $= xy$

$$\lambda_{\infty}(A_x B_y) = x \lambda_{\infty}(A^{+y}) + y \lambda_{\infty}(B^{-x})$$

#

$$\lambda_{eq}^{\infty} = \frac{\lambda_m^{\infty}}{V.f.} \Rightarrow \lambda_m^{\infty} = \lambda_{eq}^{\infty} \cdot V.f.$$

$$\lambda_m^{\infty}(A_x B_y) = \lambda_{eq}^{\infty}(A_x B_y) \cdot XY$$

given

# Molar Conductance of cation ( $A^{+y}$ ) =  $\lambda_m^{\infty}(A^{+y})$ Molar conductance of anion ( $B^{-x}$ ) =  $\lambda_m^{\infty}(B^{-x})$ 

$$\lambda_{eq}^{\infty}(A_x B_y) = ?$$

$$\Lambda_{\text{eq}}^{\infty}(A^+Y^-) = \frac{\Lambda_{\text{m}}^{\infty}(A^+Y^-)}{y}$$

$y = \text{v.f. (Charge on cation)}$   
of cation

$$\Lambda_{\text{eq}}^{\infty}(B^-X^+) = \frac{\Lambda_{\text{m}}^{\infty}(B^-X^+)}{x}$$

$x = \text{v.f. (Charge on anion)}$   
of anion

$$\# \quad \Lambda_{\text{eq}}^{\infty}(A_xB_y) = \frac{\Lambda_{\text{m}}^{\infty}(A^+Y^-)}{y} + \frac{\Lambda_{\text{m}}^{\infty}(B^-X^+)}{x}$$

Equivalent conductance of  $A_xB_y$  in terms of molar conductance.

Ques. Limiting ionic conductance (Conductance at  $\infty$  dilution)

of  $H^+$  &  $SO_4^{2-}$  are  $360 \text{ S cm}^2 \text{ eq}^{-1}$  &  
 $80 \text{ S cm}^2 \text{ eq}^{-1}$  respectively. Calc.  
Equivalent & molar conductance of  
 $H_2SO_4$  at  $\infty$ -dilution

v.f = 2

Sol given:  $\lambda_{eq}^\infty(H^+) = 360 \text{ S cm}^2 \text{ eq}^{-1}$

$$\lambda_{eq}^\infty(SO_4^{2-}) = 80 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{eq}^\infty(H_2SO_4) = 360 + 80 = 440$$

$$\lambda_m^\infty(H_2SO_4) = 440 \times 2 = 880$$

Q.2. limiting ionic conductance of  $Al^{3+}$  &  $SO_4^{2-}$  ion are  $189 \text{ S cm}^2 \text{ mol}^{-1}$  &  $160 \text{ S cm}^2 \text{ mol}^{-1}$

v.f. = 6 ← Cal equivalent & molar conductance of  $Al_2(SO_4)_3$  at  $\infty$ -dilution.

$$\lambda_{\text{sol}}^{\infty} = \lambda_{\text{given}}^{\infty} + \lambda_{\text{ion}}^{\infty}$$

$$\lambda_{\text{m}}^{\infty}(Al^{3+}) = 189 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{\text{eq}}^{\infty}(Al^{3+}) = \frac{189}{3} = 63 \text{ eq}^{-1}$$

$$\lambda_{\text{m}}^{\infty}(SO_4^{2-}) = 160 \text{ S cm}^2 \text{ mol}^{-1}$$

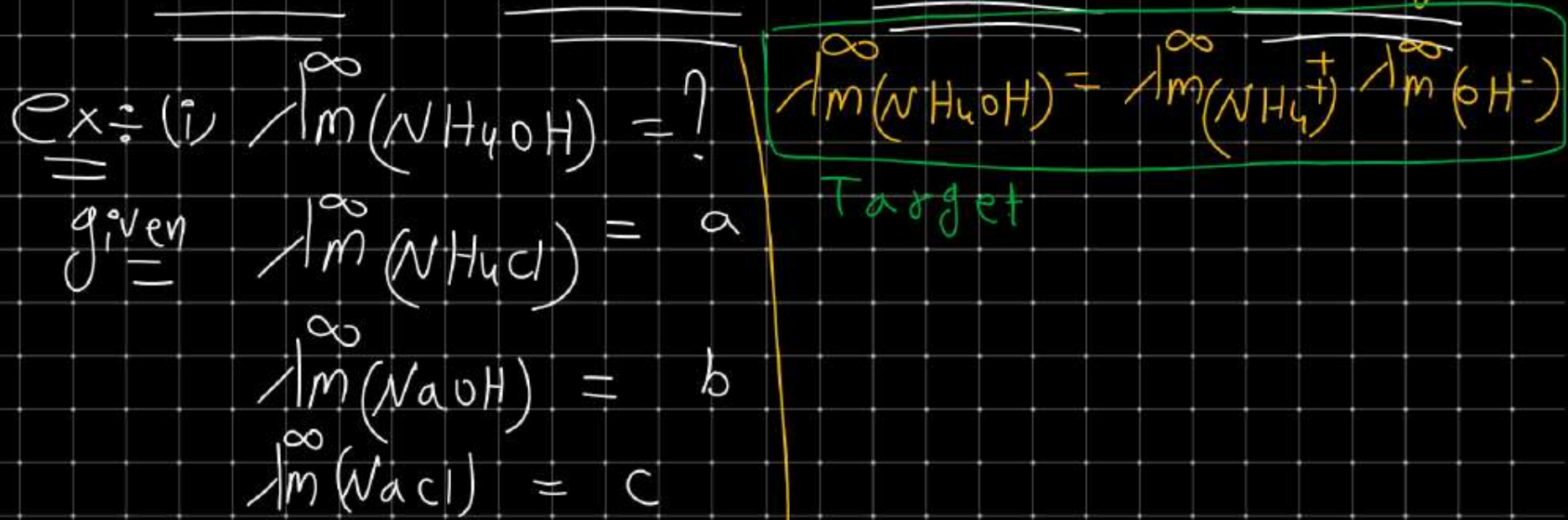
$$\lambda_{\text{eq}}^{\infty}(SO_4^{2-}) = \frac{160}{2} = 80$$

$$\lambda_{\text{eq}}^{\infty} Al_2(SO_4)_3 = 63 + 80 = 143$$

$$\lambda_{\text{m}}^{\infty} Al_2(SO_4)_3 = 143 \times 6 = 858 \text{ S cm}^2 \text{ mol}^{-1}$$

## Applications of Kohlrausch Law

(1) To determine molar conductance of weak electrolyte



$$\overset{\infty}{\lambda}m(\text{NH}_4\text{Cl}) = \overset{\infty}{\lambda}m(\text{NH}_4^+) + \overset{\infty}{\lambda}m(\text{Cl}^-) - \textcircled{1}$$

$$\overset{\infty}{\lambda}m(\text{NaOH}) = \cancel{\overset{\infty}{\lambda}m(\text{Na}^+)} + \overset{\infty}{\lambda}m(\text{OH}^-) - \textcircled{2}$$

$$\overset{\infty}{\lambda}m(\text{NaCl}) = \cancel{\overset{\infty}{\lambda}m(\text{Na}^+)} + \cancel{\overset{\infty}{\lambda}m(\text{Cl}^-)} - \textcircled{3}$$

$$\text{Ca } \textcircled{1} + \textcircled{2} - \textcircled{3}$$

$$\overset{\infty}{\lambda}m(\text{NH}_4\text{OH}) = \overset{\infty}{\lambda}m(\text{NH}_4\text{Cl}) + \overset{\infty}{\lambda}m(\text{NaOH}) - \overset{\infty}{\lambda}m(\text{NaCl})$$

$$\boxed{\overset{\infty}{\lambda}m(\text{NH}_4\text{OH}) = a + b - c}$$



Ex: (ii)  $\underline{\underline{m_{Ba(OH)_2}^\infty = ?}}$

given:  $\underline{\underline{m_{BaCl_2}^\infty = x}}$  — (1)

$2 \times \underline{\underline{m_{NaOH}^\infty = y}}$  — (2)

$2 \times \underline{\underline{m_{NaCl}^\infty = z}}$  — (3)

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$e_w(1) + 2e_w(2) - 2 \times e_w(3)$

$$m_{Ba(OH)_2}^\infty = m_{Ba^{2+}}^\infty + 2 m_{(OH)^-}^\infty$$

$$m_{Ba(OH)_2}^\infty = x + 2y - 2z$$

(2) To determine degree of dissociation ( $\alpha$ ) of weak electrolyte -

$$\alpha = \frac{\lambda_{eq}}{\lambda_{\infty}} = \frac{\lambda_m / v.f}{\lambda_{\infty}}$$

OR

$$\alpha = \frac{\lambda_m}{\lambda_{\infty}}$$

(3) To determine dissociation constant  
( $K_a$  or  $K_b$ ) :-

for weak acid,  $K_a = \frac{C\alpha^2}{1-\alpha}$

for weak base,  $K_b = \frac{C\alpha^2}{1-\alpha}$

\* If  $\alpha \ll 1$  then  $1-\alpha \approx 1$

$$K_a/K_b = C\alpha^2$$

(4) To determine solubility ( $S$ ) & solubility product ( $K_{sp}$ )

# molar conc. of saturated soln is  $K/a$  solubility.

# Saturated soln of sparingly soluble salt is considered at infinite dilution

for Saturated soln



$$\boxed{\frac{1}{m} = \frac{K \cdot 1000}{S}} \rightarrow \text{Solubility}$$

$K_{sp}$  of AB type electrolyte -



$$K_{sp} = S^2$$